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54 Alkylidenenorbornene polymer and process for producing the same.

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EP 0 492 982 B1

Description

The present invention relates to a novel alkylidenenorbornene polymer excellent in heat resistance, light resistance, transparency and moisture resistance and useful as an optical material and to a process for producing the same.

Optical polymeric materials mainly used up to now are poly(methyl methacrylate) and polycarbonate. These polymers, however, have drawbacks in that the former shows high water absorption and insufficient heat resistance, while the latter gives injection moldings with high birefringence. Accordingly, it is increasingly difficult for these polymers to meet the requirements for optical polymeric materials which are becoming increasingly severe.

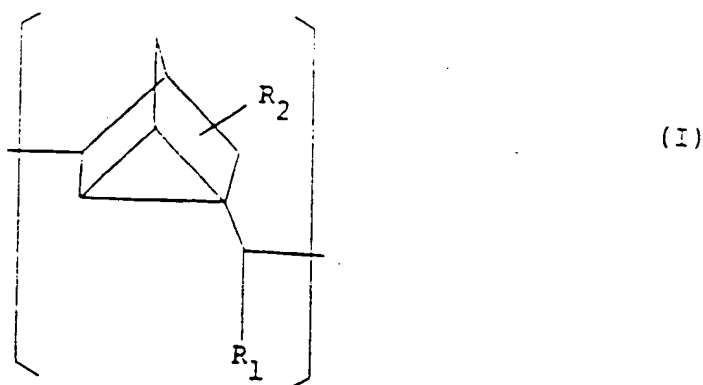
As polymeric materials improved in such drawbacks, there have been developed polymers which use polycyclic norbornene-group monomers. For example, it has been disclosed in Japanese Patent Application Kokai (Laid-open) Nos. 60-26,024, 64-24,826, 60-168,708, 61-115,912, 61-120,816 and others that thermoplastic saturated norbornene polymers as hydrogenation products of ring-opening polymers of norbornene monomers and addition-type copolymers of norbornene monomers with ethylene have excellent characteristic properties as optical disk substrate materials.

In the prior arts mentioned above, polycyclic monomers such as tetracyclododecenes must be used as the norbornene monomer to secure high heat resistance required for optical materials. However, the preparation of polycyclic monomers is not always easy. The polycyclic monomers are usually synthesized by addition reaction of norbornenes with cyclopentadiene under heating. While they must be separated and purified by means of distillation since the reaction product contains a substantial amount of byproducts such as oligomers of cyclopentadiene, the separation and purification can be performed only with difficulty. Consequently, polycyclic monomers, particularly tetracyclododecene derivatives, are very expensive and not advantageous for industrial use. Also, they are restricted as to the kinds of available monomers.

On the other hand, it is described in *La Chimica et l'Industria*, 45, 1,529 (1963) and *Macromolecular Chemistry, Rapid Communication*, 1, 467 (1980) that, among bicyclic norbornenes, 5-methylidenenorbornene, which has a methylidene group, undergoes transannular polymerization to give a saturated linear polymer. However, 5-methylidenenorbornene used as the monomer is still more difficultly available than said tetracyclododecenes and further has the drawback of being apt to form gels in polymerization. Moreover, the polymer described in *La Chimica et l'Industria*, 45, 1529 (1963) is crystalline and lacking in optical isotropy, so that it cannot be used as an optical material.

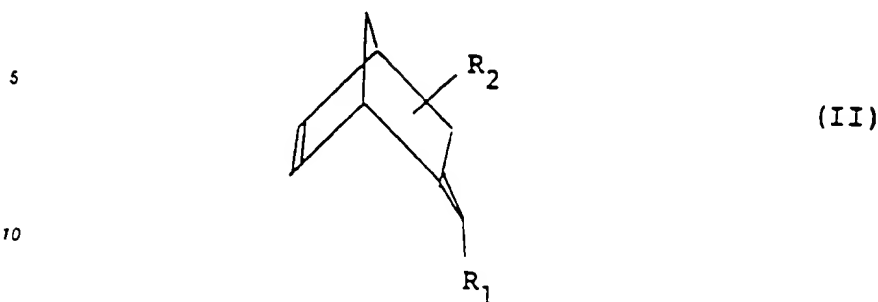
The present inventors have made extensive study with the aim of developing optical polymers using norbornene monomers that can be obtained more inexpensively. As the result, it has been found that polymers obtained by polymerization of specific alkylidenenorbornenes used as the monomer component with the aid of cationic polymerization catalysts contain no gel and are excellent in transparency, heat resistance, light resistance and moisture resistance. The present invention has been attained on the basis of above finding.

According to the present invention, there are provided a novel alkylidenenorbornene polymer comprising as the main component of the principal chain the structural unit represented by the formula



wherein R_1 denotes an alkyl group and R_2 denotes a hydrogen atom or an alkyl group, and a process for producing said alkylidenenorbornene polymer which comprises polymerizing alkylidenenorbornenes in the presence of a cationic polymerization catalyst.

The alkylidenenorbornenes used in the present invention are compounds represented by the formula



wherein R_1 denotes an alkyl group and R_2 denotes a hydrogen atom or an alkyl group. Preferably, R_1 is a C_1 - C_4 alkyl group and R_2 is a C_1 - C_4 alkyl group or a hydrogen atom. More preferably, R_1 is a methyl group and R_2 is a methyl group or a hydrogen atom. As specific examples, mention may be made of 5-ethylidenenorbornene, 5-propylidenenorbornene, 5-*i*-propylidenenorbornene and 5-*i*-butylidenenorbornene. These monomers can be easily obtained by the isomerization of alkenynorbornene derivatives obtainable by the reaction of dienes, e.g. butadiene, isoprene, 1,3-pentadiene and 3-methyl-1,3-pentadiene, with dicyclopentadiene. These monomers may be used either alone or as a mixture of two or more thereof.

In the present specification, the term "norbornene" includes also norbornene derivative.

In the polymerization it is also possible, in order to improve the characteristic properties as processability, flexibility and mechanical strength of the polymer obtained, to polymerize mixtures of alkylidenenorbornenes with other cationically polymerizable monomers than alkylidenenorbornenes. Specific examples of such cationically polymerizable monomers which can be used as mixtures include monoolefins such as propylene, isobutene, 2-methyl-1-butene and 2-methyl-1-pentene, diolefins such as butadiene, isoprene and 1,3-pentadiene, vinylaromatic compounds such as styrene, α -methylstyrene and vinylnaphthalene, and cyclic ethers such as ethylene oxide, propylene oxide, trimethylene oxide, dioxane, trioxane, cyclohexene oxide, styrene oxide, epichlorohydrin, glycidyl phenyl ether, furan and tetrahydrofuran.

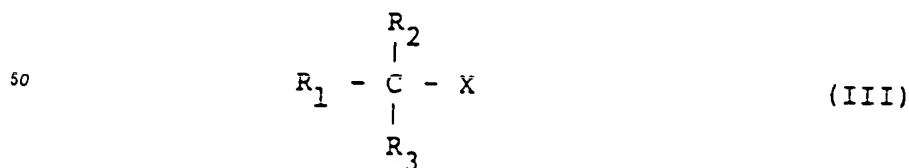
The content of the structural unit represented by the formula I in the alkylidenenorbornene polymer of the present invention is usually at least 50% by weight, preferably at least 60% by weight, more preferably at least 70% by weight. As the content of the structural unit represented by the formula I in the alkylidenenorbornene polymer of the present invention decreases, the glass transition temperature of the polymer lowers.

The cationic polymerization catalyst used in the present invention may be conventionally used ones. As specific examples, there may be mentioned, for Lewis acids, metal halides such as $AlCl_3$, $AlBr_3$, BCl_3 , BF_3 , $TiCl_4$, $TiBr_4$, $FeCl_3$, $FeCl_2$, $SnCl_2$ and $SnCl_4$ and, for protonic acids, hydroacids such as HCl, HF and HBr and oxoacids such as H_2SO_4 , H_3BO_3 , $HClO_4$ and CH_3COOH . Particularly preferred are Lewis acids, among which halogen compounds, particularly chlorides, of boron or titanium are more preferred.

When a catalyst comprising at least one selected from Lewis acids and protonic acids is used as the cationic polymerization catalyst, it is used in a range of amount of 0.000001-1 mole, preferably 0.00001-0.5 mole, per mole of the polymerizable monomer composition.

Particularly when a Lewis acid is used, it is preferably used in combinations with an initiator compound which are known as so-called Kennedy catalysts in cationic living polymerization of olefins.

The initiator compound used herein is a compound represented by the formula



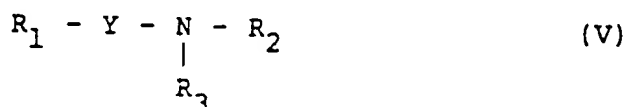
wherein R_1 denotes an aliphatic or aromatic hydrocarbon group or a substitution product thereof, R_2 and R_3 each independently denote a lower aliphatic hydrocarbon group or an aromatic hydrocarbon group, X denotes a hydroxyl group, an alkoxyl group, an acyloxy group or a halogen and n denotes a natural number. Specific examples thereof include tert-butanol, 2,4,4-trimethyl-2-methoxypentane, 2-phenyl-2-pro-

panol, 2-methoxy-2-phenylpropane, 2,5-dimethyl-dihydroxyhexane, 2,5-dimethyl-2,5-diacetoxyhexene, 2,5-dimethyl-2,5-dichlorohexyne, 2,4,4,6-tetramethyl-2,6-dihydroxyheptane, 1,3-bis(2-acetoxy-2-propyl)benzene, 1,4-bis(2-methoxy-2-propyl)benzene, 1,3,4-tris(2-bromo-2-propyl)benzene and 1,3,5-tris(2-methoxy-2-propyl)benzene.

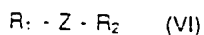
When the catalyst is used in the form of so-called Kennedy catalyst, particularly when a titanium halide, in particular $TiCl_4$ is used, it is more preferable to use an electron donative compound together therewith. The electron donative compound used in the present invention is a compound represented by the formula



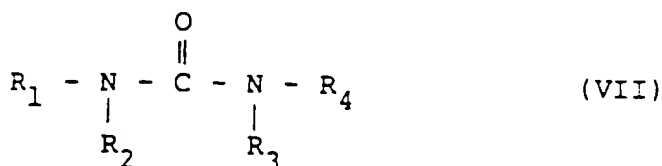
wherein R_1 , R_2 and R_3 each independently denote a hydrogen atom, an aliphatic hydrocarbon group or an aromatic hydrocarbon group and W denotes N, NO, P, PO or PS, provided that said aromatic hydrocarbon group may be a heterocyclic ring containing a so-called hetero atom such as nitrogen, oxygen and sulfur and R_1 , R_2 and R_3 may form a ring structure, or the formula



wherein R_1 , R_2 and R_3 each independently denote a hydrogen atom, an aliphatic hydrocarbon group or an aromatic hydrocarbon group and Y denotes CO or SO_2 , provided that said aromatic hydrocarbon group may be a heterocyclic ring containing a so-called hetero atom such as nitrogen, oxygen and sulfur and R_1 , R_2 and R_3 may form a ring structure, or the formula



wherein R_1 and R_2 each independently denote a hydrogen atom, an aliphatic hydrocarbon group or an aromatic hydrocarbon group and Z denotes O, CO, COO, OCOO, S, SO or SO_2 , provided that said aromatic hydrocarbon group may be a heterocyclic ring containing a so-called hetero atom such as nitrogen, oxygen and sulfur and R_1 and R_2 may form a ring structure, or the formula



wherein R_1 , R_2 , R_3 and R_4 each independently denote a hydrogen atom, an aliphatic hydrocarbon group or an aromatic hydrocarbon group, provided that said aromatic hydrocarbon group may be a heterocyclic ring containing a so-called hetero atom such as nitrogen, oxygen and sulfur and R_1 , R_2 , R_3 and R_4 may form a ring structure.

Specific examples of the electron donative compound represented by the formula (IV) include diethylamine, triethylamine, pyridine, thiazole, guanidine, N-methylmorpholine oxide, triphenylphosphine and triphenyl phosphate. Specific examples of the electron donative compound represented by the formula (V) include acetamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, maleimide, benzenesulfonamide and saccharin. Specific examples of the electron donative compound represented by the formula (VI) include diethyl ether, phenetole, tetrahydrofuran, pyran, dioxane, tetrahydrothiophene, benzaldehyde, acetic acid, benzoic acid, succinic anhydride, acetone, acetonitrile and ethyl acetate. Specific examples of the electron donative compound represented by the formula (VII) include tetramethylurea, dicyclohexylurea and N,N-dimethylimidazolidinone. Particularly preferred among these compounds are

tertiary amines or aromatic amines such as triethylamine and pyridine, phosphorus compounds such as triphenylphosphine and triphenyl phosphate, carboxylic acid amides such as N,N-dimethylformamide and N,N-dimethylacetamide, ethers such as diethyl ether and tetrahydrofuran, sulfoxides such as dimethyl sulfoxide, ketones such as acetone, and esters such as ethyl acetate.

The amount of the initiator compound to be used is 0.01-1 mole in terms of the functional group of the initiator compound (that is, the hydroxyl group, alkoxy group, acyloxy group or halogen denoted by X in the formula (III)) per mole of the Lewis acid. The amount of the electron donative compound to be used is 0.01-100 moles per mole of the functional group of the initiator compound.

Although the polymerization of the present invention may be performed without using a solvent, it is usually preferable to use halogenated hydrocarbon solvents such as methyl chloride, methylene chloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane and 1,1,2-trichloroethene, hydrocarbon solvents such as pentane, hexane, heptane, octane, cyclopentane, cyclohexane, decalin and methylcyclohexane, aromatic solvents such as benzene, toluene and xylene, or other suitable solvents.

The polymerization is usually conducted in a temperature range of -150°C to 100°C, preferably -100°C to 50°C.

The alkylidenenorbornene polymer of the present invention contains virtually no olefinic bonds, is amorphous, optically isotropic and transparent, and has a higher glass transition temperature as compared with ring-opening polymers of the same monomer. For example, in the case of polymers comprising solely the structural unit represented by the formula I, polymers having a glass transition temperature of 150°C or more can be easily obtained. Though the glass transition temperature can be adjusted by use of a suitable comonomer, it is preferably selected at 100°C or more, more preferably 120°C or more. The range of the molecular weight is, in terms of intrinsic viscosity determined in decalin at 50°C, 0.1-20 dl/g, preferably 0.2-10 dl/g, more preferably 0.4-5 dl/g. As the intrinsic viscosity decreases, the mechanical strength of the molded articles decreases. As the intrinsic viscosity increases, the melt viscosity increases and the processability becomes poorer. The polymer of the present invention contains substantially no gel and can be dissolved in suitable solvents. For example, it dissolves completely in decalin at 50°C. Further, since the polymer of the present invention is obtained by polymerisation of hydrocarbon monomers, it is excellent in moisture resistance. Its water absorption after immersion in water at 25°C for 24 hours is 0.2% or less, preferably 0.1% or less.

The alkylidenenorbornene polymer of the present invention can be processed by conventional methods. In the processing, various additives may be added for the purpose of improving processability and properties of the product, which include, for example, fibrous or particulate fillers, antioxidants, light stabilizers, ultra-violet absorbers, antistatic agents, lubricants, flame retardants, pigment, dyes, antiblocking agents, other kinds of polymers, and oligomers.

The alkylidenenorbornene polymer of the present invention is amorphous, has a high glass transition temperature and is excellent in heat resistance, light resistance, moisture resistance, and transparency, so that it is useful as various formed articles in a wide field of applications including optical materials. For example, it can be used for optical materials, such as optical disks, optical lenses, optical cards, optical fibers and liquid crystal display device substrates, electric or electronic uses such as printed boards, high frequency circuit boards, insulating materials and the like, medical uses, chemical materials, structural materials such as film, sheeting and various instrument parts and housings, building materials, and in other various fields.

Examples

The present invention will be described in more detail below with reference to Examples, in which "part" means part by weight unless otherwise specified. The examples are provided by way of illustration and not limitation.

Example 1

In a reactor flushed with nitrogen, were placed 900 parts of methylene chloride and 100 parts of 5-ethylidenenorbornene. While the temperature was being kept at -50°C, 0.5 part of 2-methoxy-2-phenylpropane and successively 3.8 parts of TiCl_3 were added thereto, and the whole was reacted at -50°C for 2 hours. The reaction solution was poured into 5,000 parts of methanol at room temperature to coagulate the polymer formed. The precipitate was separated by filtration and dried under reduced pressure to obtain 63 parts of amorphous polymer.

The polymer obtained dissolved completely in decalin. It had an intrinsic viscosity of 0.57 dl/g as determined in decalin at 50 °C and a glass transition temperature of 163 °C as determined by DSC analysis. Its infrared spectrum showed a strong absorption band at 850 cm⁻¹ attributed to transannular polymerization (cf. *La Chimica et l'Industria*, 45, 1529 (1963)). Analysis by proton NMR spectrum in deuterio chloroform showed at 0.4-2.6 ppm the presence of protons of saturated hydrocarbons amounting to 98.9% of the total protons. Though a very small amount of olefinic protons was observed at 4.8-5.6 ppm, the amount was only 1.1% relative to the total protons, showing that the content of components having unsaturated groups was very small.

The polymer was compression-molded at 210 °C to prepare test pieces 5 cm square and 2 mm thick. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 2

In the same manner as in Example 1 except for using 90 parts of 5-ethylidenenorbornene and 10 parts of styrene in place of 5-ethylidenenorbornene alone, 72 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.61 dl/g as determined in decalin at 50 °C. Its glass transition temperature determined by DSC analysis was a single point of 155 °C. The infrared absorption spectrum showed at 850 cm⁻¹ a strong absorption band based on transannular polymer. Analysis by proton NMR spectrum in deuterio chloroform showed saturated hydrocarbon protons at 0.4-2.7 ppm and phenyl group protons at 6.8-7.1 ppm in an area ratio of 95:5. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with styrene. From the area ratio of saturated hydrocarbon protons to phenyl group protons, it was revealed that the ratio of the structural units derived from styrene to the structural units represented by the formula (I) in the copolymer was about 11 to 89.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 3

In the same manner as in Example 1 except for using 50 parts of 5-ethylidenenorbornene and 50 parts of styrene in place of 5-ethylidenenorbornene alone, 69 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.59 dl/g as determined in decalin at 50 °C. Its glass transition temperature determined by DSC analysis was a single point of 132 °C. The infrared absorption spectrum showed at 850 cm⁻¹ a strong absorption band based on transannular polymer. Analysis by proton NMR spectrum in deuterio chloroform showed saturated hydrocarbon protons at 0.4-2.7 ppm and phenyl group protons at 6.8-7.1 ppm in an area ratio of 84:16. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with styrene. From the area ratio of saturated hydrocarbon protons to phenyl group protons, it was revealed that the ratio of the structural units derived from styrene to the structural units represented by the formula (I) in the copolymer was about 34 to 66.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 4

In the same manner as in Example 1 except for using 95 parts of 5-ethylidenenorbornene and 5 parts of cyclohexene oxide in place of 5-ethylidenenorbornene alone, 48 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and showed an intrinsic viscosity of 0.45 dl/g as determined in decalin at 50 °C and a glass transition temperature of 148 °C by DSC analysis. The infrared absorption spectrum showed at 850 cm⁻¹ a strong absorption band based on transannular polymer. Analysis by proton NMR spectrum in deuterio chloroform showed saturated hydrocarbon protons at 0.4-3.0 ppm amounting to 99.3% of the total protons. Though a very small amount of olefinic protons was observed at 4.8-5.6 ppm, the amount was only 0.7% relative to the total protons, showing that the content of

components having unsaturated groups was very small.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.1% or less.

Example 5

In the same manner as in Example 1 except for using 90 parts of 5-ethylidenenorbornene and 10 parts of α -methylstyrene in place of 5-ethylidenenorbornene alone, 95 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.59 dl/g as determined in decalin at 50 °C. Its glass transition temperature determined by DSC analysis was a single point of 160 °C. The infrared absorption spectrum showed at 850 cm^{-1} a strong absorption band based on transannular polymer. Analysis by proton NMR spectrum in deuterio chloroform showed saturated hydrocarbon protons at 0.4-2.7 ppm and phenyl group protons at 6.8-7.1 ppm in an area ratio of 96:4. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with α -methylstyrene. From the area ratio of saturated hydrocarbon protons to phenyl group protons, it was revealed that the ratio of the structural units derived from α -methylstyrene to the structural units represented by the formula (I) was about 12 to 88.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 6

In the same manner as in Example 1 except for using 75 parts of 5-ethylidenenorbornene and 25 parts of α -methylstyrene in place of 5-ethylidenenorbornene alone, 93 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.56 dl/g as determined in decalin at 50 °C. Its glass transition temperature determined by DSC analysis was a single point of 160 °C. The infrared absorption spectrum showed at 850 cm^{-1} a strong absorption band based on transannular polymer. Analysis by proton NMR spectrum in deuterio chloroform showed saturated hydrocarbon protons at 0.4-2.7 ppm and phenyl group protons at 6.8-7.1 ppm in an area ratio of 90:10. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with α -methylstyrene. From the area ratio of saturated hydrocarbon protons to phenyl group protons, it was revealed that the ratio of the structural units derived from α -methylstyrene to the structural units represented by the formula (I) was about 27 to 73.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 7

In the same manner as in Example 1, except for using 90 parts of 5-ethylidenenorbornene and 10 parts of isobutene in place of 5-ethylidenenorbornene alone, 80 parts of amorphous polymer was obtained.

The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.62 dl/g as determined in decalin at 50 °C. The glass transition temperature determined by DSC analysis was a single point of 142 °C. The infrared absorption spectrum showed at 850 cm^{-1} a strong absorption band based on transannular polymer. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with isobutene.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

Example 8

In the same manner as in Example 1 except for using 75 parts of 5-ethylidenenorbornene and 25 parts of isobutene in place of 5-ethylidenenorbornene alone, 75 parts of amorphous polymer was obtained.

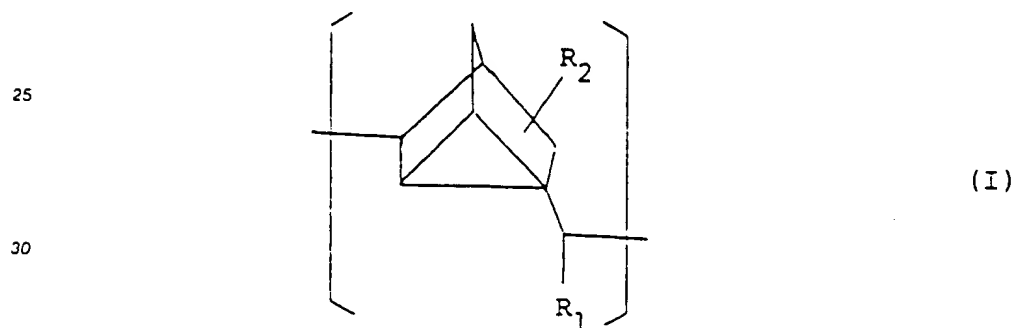
The polymer obtained dissolved completely in decalin and had an intrinsic viscosity of 0.58 dl/g as determined in decalin at 50 °C. The glass transition temperature determined by DSC analysis was a single point of 138 °C. The infrared absorption spectrum showed at 850 cm⁻¹ a strong absorption band based on transannular polymer. Virtually no olefinic protons were observed. From the fact that the glass transition temperature consisted of one point, it was revealed that the composition obtained was not a blend of homopolymers but a copolymer of 5-ethylidenenorbornene with isobutene.

Test pieces 2 mm in thickness were prepared in the same manner as in Example 1. The molded plate was tough, colorless and transparent. The light transmittance at 830 nm was as good as 90%. The water absorption after immersion in water at 25 °C for 24 hours was 0.01% or less.

From the results set forth above, it is apparent that the alkylidenenorbornene polymer of the present invention is excellent in light resistance, transparency, heat resistance and moisture resistance.

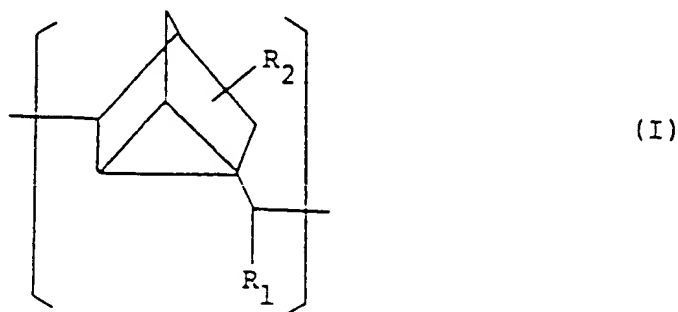
Claims

1. An alkylidenenorbornene polymer comprising as a main component of the principal chain a structural unit represented by the formula (I):

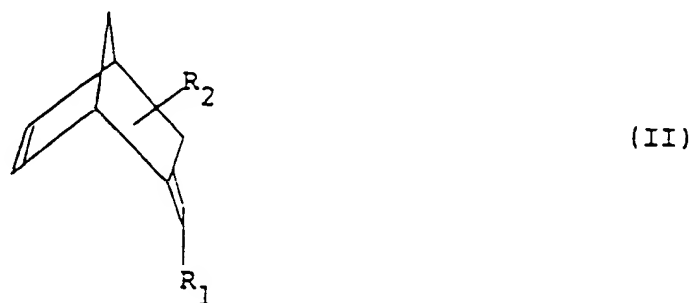


- wherein R₁ denotes an alkyl group and R₂ denotes a hydrogen atom or an alkyl group.
2. An alkylidenenorbornene polymer according to Claim 1, wherein R₁ is a C₁-4 alkyl group and R₂ is a C₁-4 alkyl group, or a hydrogen atom.
3. An alkylidenenorbornene polymer according to Claim 2, wherein R₁ is a methyl group and R₂ is a methyl group, or a hydrogen atom.
4. An alkylidenenorbornene polymer according to Claim 1, which comprises substantially the structural unit represented by the formula (I).
5. An alkylidenenorbornene polymer according to Claim 1 which has a glass transition of 150 °C or more.
6. An alkylidenenorbornene polymer according to Claim 1 which comprises as a comonomer component a cationically polymerizable monomer.
7. An alkylidenenorbornene polymer according to Claim 6, wherein said cationically polymerizable monomer is a member selected from the group consisting of monoolefins, diolefins, vinylaromatic compounds and cyclic ethers.
8. An alkylidenenorbornene polymer according to Claim 7, wherein said cationically polymerizable monomer is a member selected from the group consisting of isobutene, styrene, α-methylstyrene and cyclohexene oxide.

9. An alkylidenenorbornene polymer according to Claim 6 which contains at least 50% by weight of the structural unit represented by the formula (I).
10. An alkylidenenorbornene polymer according to Claim 9 which contains at least 70% by weight of the structural unit represented by the formula (I).
11. An alkylidenenorbornene polymer according to Claim 6 which has a glass transition temperature of 100 °C or more.
12. An alkylidenenorbornene polymer according to Claim 11 which has a glass transition temperature of 120 °C or more.
13. An alkylidenenorbornene polymer according to Claim 1 which has an intrinsic viscosity of 0,1 to 20 dl/g in decalin at 50 °C.
14. An alkylidenenorbornene polymer according to Claim 1 which has an intrinsic viscosity of 0,4 to 5 dl/g in decalin at 50 °C.
15. An alkylidenenorbornene polymer according to Claim 1 which has a water absorption of 0,2% or less after immersion in water at 25 °C for 24 hours.
16. An alkylidenenorbornene polymer according to Claim 15 which has a water absorption of 0.1% or less after immersion in water at 25 °C for 24 hours.
17. A process for producing an alkylidenenorbornene polymer comprising as a main component of the principal chain a structural unit represented by the formula (I):



wherein R_1 denotes an alkyl group and R_2 denotes a hydrogen atom or an alkyl group, which comprises polymerizing an alkylidenenorbornene represented by the formula (II):

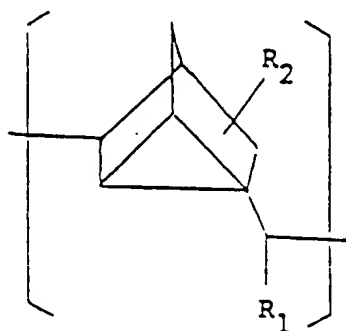


wherein R_1 and R_2 are the same meanings as defined above, or a mixture thereof with a comonomer cationically copolymerizable therewith, in the presence of a cationic polymerization catalyst.

18. A process according to Claim 18 wherein R_1 and R_2 are independently a C_1 - C_4 alkyl group, or R_2 is a hydrogen atom.
19. A process according to Claim 18 wherein R_1 is a methyl group and R_2 is a methyl group or a hydrogen atom.
20. A process according to Claim 17, wherein said cationic polymerization catalyst is a member selected from the group consisting of Lewis acids, hydroacids and oxoacids.
21. A process according to Claim 20, wherein said Lewis acids are boron halides or titan halides.
22. A process according to Claim 20, wherein an initiator compound is further used when said cationic polymerization catalyst is a Lewis acid.
23. A process according to Claim 22, wherein an electron donative compound is further used.
24. A process according to Claim 17, wherein said polymerizing is carried out at a temperature of from -150°C to 100°C .

Patentansprüche

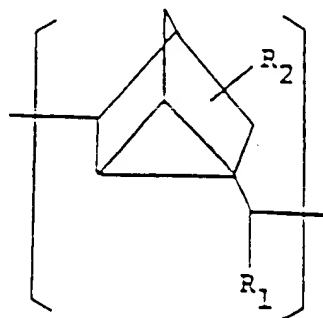
1. Alkylidennorbornenpolymer, umfassend als Hauptkomponente der Hauptkette eine Struktureinheit der Formel (I):



(I)

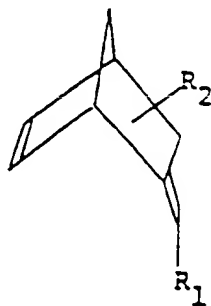
- in der R_1 einen Alkylrest bezeichnet, und R_2 ein Wasserstoffatom oder einen Alkylrest bezeichnet.
2. Alkylidennorbornenpolymer gemäß Anspruch 1, wobei R_1 ein C_1 - C_4 -Alkylrest ist, und R_2 ein C_1 - C_4 -Alkylrest oder ein Wasserstoffatom ist.
3. Alkylidennorbornenpolymer gemäß Anspruch 2, wobei R_1 eine Methylgruppe ist, und R_2 eine Methylgruppe oder ein Wasserstoffatom ist.
4. Alkylidennorbornenpolymer gemäß Anspruch 1, das im wesentlichen die Struktureinheit der Formel (I) umfaßt.
5. Alkylidennorbornenpolymer gemäß Anspruch 1, das bei 150°C oder höher eine Glasumwandlung aufweist.
6. Alkylidennorbornenpolymer gemäß Anspruch 1, das ein kationisch polymerisierbares Monomer als Comonomerkomponente umfaßt.
7. Alkylidennorbornenpolymer gemäß Anspruch 6, wobei das kationisch polymerisierbare Monomer ausgewählt ist aus Monoolefinen, Diolefinen, aromatischen Vinylverbindungen und cyclischen Ethern.

8. Alkylidennorbornenpolymer gemäß Anspruch 7, wobei das kationisch polymerisierbare Monomer ausgewählt ist aus Isobuten, Styrol, α -Methylstyrol und Cyclohexenoxid.
9. Alkylidennorbornenpolymer gemäß Anspruch 6, das wenigstens 50 Gew.-% der Struktureinheit der Formel (I) enthält.
10. Alkylidennorbornenpolymer gemäß Anspruch 9, das wenigstens 70 Gew.-% der Struktureinheit der Formel (I) enthält.
11. Alkylidennorbornenpolymer gemäß Anspruch 6, das eine Glasumwandlungstemperatur von 100 °C oder höher aufweist.
12. Alkylidennorbornenpolymer gemäß Anspruch 11, das eine Glasumwandlungstemperatur von 120 °C oder höher aufweist.
13. Alkylidennorbornenpolymer gemäß Anspruch 1, das eine Grenzviskosität von 0,1 bis 20 dl/g in Decalin bei 50 °C aufweist.
14. Alkylidennorbornenpolymer gemäß Anspruch 1, das eine Grenzviskosität von 0,4 bis 5 dl/g in Decalin bei 50 °C aufweist.
15. Alkylidennorbornenpolymer gemäß Anspruch 1, das nach 24-stündigem Eintauchen in Wasser bei 25 °C eine Wasserabsorption von 0,2 % oder weniger aufweist.
16. Alkylidennorbornenpolymer gemäß Anspruch 15, das nach 24-stündigem Eintauchen in Wasser bei 25 °C eine Wasserabsorption von 0,1 % oder weniger aufweist.
17. Verfahren zur Herstellung eines Alkylidennorbornenpolymers, umfaßend als Hauptkomponente der Hauptkette eine Struktureinheit der Formel (I):



(I)

in der R₁ einen Alkylrest bezeichnet, und R₂ ein Wasserstoffatom oder einen Alkylrest bezeichnet, das das Polymerisieren eines Alkylidennorbornens der Formel (II):



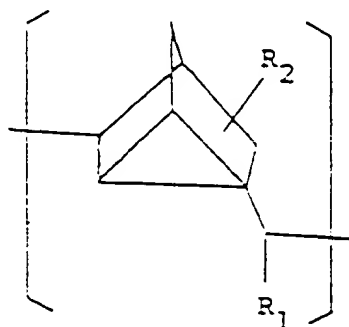
(II)

in der R_1 und R_2 dieselben Bedeutungen aufweisen, wie vorstehend definiert, oder eines Gemisches davon mit einem Comonomer, das damit kationisch copolymerisierbar ist, in Gegenwart eines kationischen Polymerisationskatalysators umfaßt.

- 5 18. Verfahren gemäß Anspruch 17, wobei R_1 und R_2 unabhängig voneinander ein C_1 - C_4 -Alkylrest sind, oder R_2 ein Wasserstoffatom ist.
19. Verfahren gemäß Anspruch 18, wobei R_1 eine Methylgruppe ist, und R_2 eine Methylgruppe oder ein Wasserstoffatom ist.
- 10 20. Verfahren gemäß Anspruch 17, wobei der kationische Polymerisationskatalysator ausgewählt ist aus Lewis-Säuren, Hydrosäuren und Oxosäuren.
21. Verfahren gemäß Anspruch 20, wobei die Lewis-Säuren Borhalogenide oder Titanhalogenide sind.
- 15 22. Verfahren gemäß Anspruch 20, wobei zusätzlich eine Initiatorverbindung verwendet wird, wenn der kationische Polymerisationskatalysator eine Lewis-Säure ist.
23. Verfahren gemäß Anspruch 22, wobei zusätzlich eine elektronenspendende Verbindung verwendet wird.
- 20 24. Verfahren gemäß Anspruch 17, wobei das Polymerisieren bei einer Temperatur von -150°C bis 100°C durchgeführt wird.

25 Revendications

1. Polymère d'alkylidènenorbornène comprenant comme composant principal de la chaîne principale une unité structurale représentée par la formule (I) :

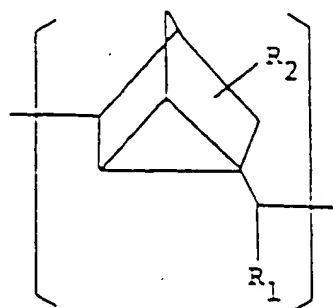


(I)

dans laquelle R_1 signifie un groupe alkyle et R_2 signifie un atome d'hydrogène ou un groupe alkyle.

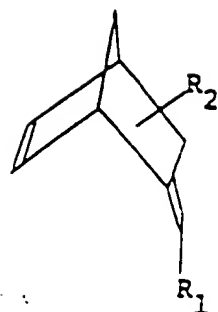
- 45 2. Polymère d'alkylidènenorbornène selon la revendication 1, dans lequel R_1 est un groupe alkyle en C_1 - C_4 et R_2 est un groupe alkyle en C_1 - C_4 , ou un atome d'hydrogène.
3. Polymère d'alkylidènenorbornène selon la revendication 2, dans lequel R_1 est un groupe méthyle et R_2 est un groupe méthyle, ou un atome d'hydrogène.
- 50 4. Polymère d'alkylidènenorbornène selon la revendication 1, qui comprend substantiellement une unité structurale représentée par la formule (I).
5. Polymère d'alkylidènenorbornène selon la revendication 1 qui a une transition vitreuse de 150°C ou plus.
- 55 6. Polymère d'alkylidènenorbornène selon la revendication 1 qui comprend comme composant comonomère un monomère polymérisable cationiquement.

7. Polymère d'alkylidènenorbornène selon la revendication 6, dans lequel ledit monomère cationiquement polymérisable est un membre sélectionné dans le groupe consistant en monooléfines, dioléfinés, composés vinylaromatiques et éthers cycliques.
8. Polymère d'alkylidènenorbornène selon la revendication 7, dans lequel ledit monomère cationiquement polymérisable est un membre sélectionné dans le groupe consistant en oxyde d'isobutène, de styrène, d' α -méthylstyrène et de cyclohexène.
9. Polymère d'alkylidènenorbornène selon la revendication 6 qui contient au moins 50% en poids de l'unité structurale représentée par la formule (I).
10. Polymère d'alkylidènenorbornène selon la revendication 9 qui contient au moins 70% de l'unité structurale représentée par la formule (I).
11. Polymère d'alkylidènenorbornène selon la revendication 6 qui a une température de transition vitreuse de 100 °C ou plus.
12. Polymère d'alkylidènenorbornène selon la revendication 11 qui a une température de transition vitreuse de 120 °C ou plus.
13. Polymère d'alkylidènenorbornène selon la revendication 1 qui a une viscosité intrinsèque de 0,1 à 20 dl/g dans la décالية à 50 °C.
14. Polymère d'alkylidènenorbornène selon la revendication 1 qui a une viscosité intrinsèque de 0,4 à 5 dl/g dans la décالية à 50 °C.
15. Polymère d'alkylidènenorbornène selon la revendication 1 qui a une absorption d'eau de 0,2% ou moins après immersion dans l'eau à 25 °C pendant 24 heures.
16. Polymère d'alkylidènenorbornène selon la revendication 15 qui a une absorption d'eau de 0,1% au moins après immersion dans l'eau à 25 °C pendant 24 heures.
17. Procédé de production d'un polymère d'alkylidènenorbornène comprenant comme composant principal de la chaîne principale une unité structurale représentée par la formule (I) :



(I)

dans laquelle R_1 signifie un groupe alkyle et R_2 signifie un atome d'hydrogène ou un groupe alkyle, qui comprend la polymérisation d'un alkylidènenorbornène représenté par la formule (II) :



(II)

dans laquelle R_1 et R_2 ont la même signification que défini ci-dessus, ou un mélange de ceux-ci avec un comonomère cationiquement copolymérisable avec celui-ci, en présence d'un catalyseur cationique de polymérisation.

18. Procédé selon la revendication 17 dans lequel R_1 et R_2 sont indépendamment un groupe alkyle en $C_1 - C_4$, ou R_2 est un atome d'hydrogène.
19. Procédé selon la revendication 18 dans lequel R_1 est un groupe méthyle et R_2 est un groupe méthyle ou un atome d'hydrogène.
20. Procédé selon la revendication 17, dans lequel ledit catalyseur cationique de polymérisation est un membre sélectionné dans le groupe consistant en acides de Lewis, hydroacides et oxacides.
21. Procédé selon la revendication 20, dans lequel lesdits acides de Lewis sont des halogénures de bore ou des halogénures de titane.
22. Procédé selon la revendication 20, dans lequel un composé initiateur est de plus utilisé quand ledit catalyseur cationique de polymérisation est un acide de Lewis.
23. Procédé selon la revendication 22, dans lequel un composé donneur d'électrons est de plus utilisé.
24. Procédé selon la revendication 17, dans lequel ladite polymérisation est mise en oeuvre à une température de -150°C à 100°C .